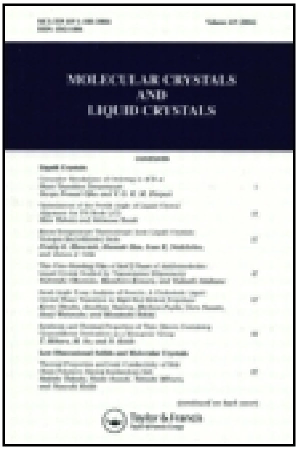

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Thermotropic Mesomorphism in a Series of Copper β-Diketonates and Their Ligands

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A homologous series of bis[1-(*p*-*n*-alkylphenyl)3-(*p*-*n*-alkyloxyphenyl)propane 1,3-dionato]copper(II) complexes have been synthesised and their mesogenic properties are studied. A few of the ligands which are used to obtain these chelates also exhibit mesophases. A plot of the mesophase → isotropic transition points versus the molecular weight of the chelates gives smooth curve relationship. Optical texture and preliminary x-ray studies indicate that the mesophase of the chelates are lamellar in nature.

Keywords: β*-diketone, chelate, ligand, lamellar*

INTRODUCTION

In recent years the synthesis of compounds containing transition metals has resulted in the observation of a variety of mesophases. In particular copper(II) and palladium(II) atoms, which form a square planar geometry, have been utilised widely. To obtain these chelates different types of ligands have been used, for e.g., o-hydroxy substituted Schiff's bases, azo compounds, β-diketones, etc. The type of mesophase obtained depends on the nature of the ligand and in certain cases non-mesogenic ligands have given rise to mesogenic complexes. Since the early work of A. M. Giroud and her co-workers[1,2] on mesogenic transition metal complexes, several different types of mesophases have been obtained. These include both uniaxial[2–5] and biaxial nematic phases,[6] smectic,[7] columnar[8] and discotic lamellar phases.[9] In a preliminary communication, we had earlier reported[10] the mesomorphic properties of a few disk-like copper β-diketonates. We believe that some of the data presented there are in error. We have reprepared these compounds and in this paper report the mesogenic properties of this homologous series of bis[1-(*p*-*n*-alkylphenyl)3-(*p*-*n*-alkyloxyphenyl) propane 1,3-dionato]copper(II) complexes and a few of their ligands.

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EXPERIMENTAL

The transition temperatures were determined by sandwiching samples between a glass slide and a cover slip under a polarising microscope (Leitz Laborlux 12 POL) equipped with a heating stage and a controller (Mettler FP52 and FP5 respectively). The enthalpies of transitions were calculated from thermograms obtained on a differential scanning calorimeter (Perkin-Elmer, Model DSC-2). The calorimeter was calibrated using pure indium as a standard. The infrared and electronic absorption spectra were recorded on spectrophotometers (Shimadzu 1R-435 and Hitachi U-3200 respectively). The PMR spectra were taken on a FT-NMR spectrometer (Bruker WP80SY) in deuterochloroform with tetramethylsilane as an internal standard. Satisfactory elemental analysis were obtained for all the compounds synthesised. A typical procedure for the preparation of a β-diketone and its copper complex is given below.

1-(p-n-*decylphenyl)3*-(p-n-*decyloxyphenyl)propane-1,3-dione*

In a 100 ml two-necked round bottom flask fitted with a reflux condenser and a nitrogen inlet tube was placed a mixture of *p*-*n*-decylacetophenone (2.6 g, 0.01 mole) and ethyl *p*-*n*-decyloxybenzoate (3.06 g, 0.01 mole) in dry 1,2-dimethoxyethane (60 ml). This was stirred magnetically and 60% sodium hydride (0.8 g, 0.02 mole) was added and the mixture refluxed for four hours and cooled. Ice-cold dilute hydrochloric acid (20 ml) was added and the mixture extracted with chloroform (3 × 50 ml). The chloroform solution was washed with water (3 × 50 ml) and dried (Na_2SO_4). Removal of solvent and chromatography of the residue on silica gel gave a pale yellow product. This was crystallised from acetonitrile, yield 2.02 g, m.p: 77.5°C. IR (Nujol) γ_{max} 1588 cm^{-1} and 1610 cm^{-1}; uv-vis $\lambda_{max}^{CHCl_3}$ (ϵ) 375 (19,800) 353 (33,600) 283 (8,700) 265 (9,200) 228 (12,800). NMR ($CDCl_3$) δ 0.85 (*t*, 3H-$C\underline{H}_3$), 1.0–2.0 (*m*, 32H, 16X − $C\underline{H}_2$), 2.7 (*t*, 2H, ar$C\underline{H}_2$), 4.0 (*t*, 2H, arOCH_2) 6.75 (S, 1H, —C═C$\underline{H}$—), 6.85–7.75 (*m*, 8H, ar$\underline{H}$), 17.0 (S, 1H, ═C—O$\underline{H}$). Anal. Calcd. for $C_{35}H_{52}O_3$: C, 80.77%; H, 10.0%. Found: C, 80.90%; H, 10.14%.

Bis[1-(p-n-*decylphenyl)3*-(p-n-*decyloxyphenyl)propane 1,3-dionato]copper(II)*

A mixture of 1-(*p*-*n*-decylphenyl)3-(*p*-*n*-decyloxyphenyl) propane 1,3-dione (1.04 g, 0.002 mole), powdered potassium hydroxide (0.112 g, 0.002 mole) and ethyl alcohol (10 ml) were warmed until the solution became clear. To this was added a solution of cupric chloride dihydrate (0.17 g, 0.001 mole) in ethyl alcohol (5 ml). The mixture became dark green and precipitation occurred immediately. This was stirred for four hours at room temperature and filtered. The green precipitate was collected, dissolved in chloroform (75 ml), washed with water (3 × 50 ml) and dried (Na_2SO_4). Removal of solvent and crystallisation of the residue from butan-2-one afforded green crystals of the complex. Yield 0.7 g, m.p. 94.0°C; 1R(nujol) ν_{max} 1608 cm^{-1} and 1590 cm^{-1}; uv-vis $\lambda_{max}^{CHCl_3}$ (ϵ) 383 (38,000) 358 (65,500) 303 (38,200) 275 (32,500);

Anal. Calcd. for $C_{70}H_{102}O_6Cu$: C, 76.25%; H, 9.26%. Found: C, 76.05%; H, 9.58%.

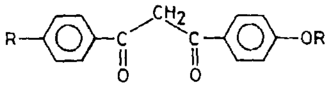
RESULTS AND DISCUSSION

The transition temperatures and the heats of transitions for the ligands 1-(*p*-*n*-alkylphenyl)3-(*p*-*n*-alkyloxyphenyl)propane 1,3-diones are shown in Table I. Compounds 1 to 5 are non-mesomorphic while the remaining do exhibit a mesophase. We had reported[10] that ligands 6 and 7 do not show any mesophase. A reexamination of these compounds showed that a mesophase does exist. The change from the crystal to the mesophase is accompanied by a small enthalpy as compared to the mesophase → isotropic transition. The latter is of the order of 7 to 8 Kcals/mole. As such, the isotropic liquid supercools considerably before the appearance of the mesophase. This value of enthalpy is large when compared with the value for other known like transitions of layered mesophases. Also, the optical texture observed for these ligands does not correspond to any of the textures seen for known smectic mesophases. Hence, this mesophase perhaps is of a new kind. The mesophase is also highly viscous, birefringent and optically biaxial.

It may be mentioned here that A. M. Giroud and J. Billard[11] and K. Ohta *et al.*[12,13] have prepared a number of β-diketones and reported that some of them do exhibit mesophases of the smectic type. However, except for the derivative with *n*-decyl chains,[11] which has been tentatively identified as smectic E, the phase type

TABLE I

Transition temperatures (°C) and heats of transitions (Kcals/mole) of 1-(*p*-*n*-alkyloxyphenyl) 3-(*p*-*n*-alkylphenyl) propane 1,3-diones



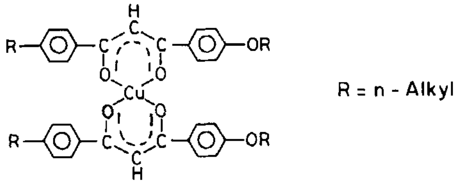
$R = C_nH_{2n+1}$

Compound number	n	K		S		I
1	4	·	67.5 5.89	—		·
2	5	·	66.0 5.28	—		·
3	6	·	68.5 6.60	—		·
4	7†	·	72.5 5.70	—		·
5	8	·	74.5 6.18	—		·
6	9	·	50.0 1.90	·	77.0 6.93	·
7	10	·	53.0 2.58	·	78.0 7.85	·
8	11	·	61.5 3.02	·	77.0 7.78	·
9	12	·	62.5 4.17	·	76.5 8.40	·

See table 2 for abbreviations; †has a crystal-crystal transition at 64.5° (3.48 Kcals/mole).

TABLE II

Transition temperatures (°C) and heats of transitions (Kcals/mole) of 1-(*p*-*n*-alkyloxyphenyl) 3-(*p*-*n*-alkylphenyl) propane 1,3-dionato]copper(II)



Compound number	*n*-Akyl	K		M		I
10	*n*-butyl	·	172.5 7.67	—		·
11	*n*-pentyl	·	158.0 9.66	—	(147.5) 4.59	·
12	*n*-hexyl	·	153.5 9.86	·	(147.0) 9.23	·
13	*n*-heptyl	·	150.3 9.97	·	(145.5) 6.32	·
14	*n*-octyl	·	80.0 9.47	·	143.0 9.30	·
15	*n*-nonyl	·	96.5 12.75	·	136.5 7.03	·
16	*n*-decyl	·	94.0 14.94	·	130.5 7.35	·
17	*n*-undecyl	·	82.0 20.38	·	127.0 9.30	·
18	*n*-dodecyl	·	81.5 25.05	·	121.0 9.16	·

Compound 11 has a crystal-crystal transition at 133° (5.71 Kcals/mole)
K: Crystal, S: Smectic phase, M: Mesophase and I: Isotropic liquid. Temperatures in parantheses indicate monotropic transitions.

of other compounds have not been established. It is noteworthy here to mention the nematogenic β-diketones reported by R. Eidenschink and L. Pohl.[14] Some of the β-diketones prepared by these authors also show smectic mesophases.

The transition temperatures and enthalpies of transitions of bis[1-(*p*-*n*-alkylphenyl)3-(*p*-*n*-alkyloxyphenyl)propane 1,3-dionato]copper(II) complexes are given in Table II. Complex 10 is non-mesogenic while complexes 11, 12 and 13 are monotropic mesomorphic. The remaining homologues which have considerably lower melting points exhibit enantiotropic mesophases. A plot of the transition temperatures versus the molecular weight/number of carbon atoms in the alkylchain is shown in Figure 1. The mesophase → isotropic transition points lie on a reasonably smooth falling curve. As observed under a polarising microscope, the mesophases are highly ordered and birefringent. Sometimes, on slow cooling of the isotropic liquid they exhibit a mosaic texture which is characteristic of the conventional smectic E phase. A typical texture of this phase is shown in Figure 2. In contrast, K. Ohta *et al.*[9] have observed a mosaic texture for the lower hom-

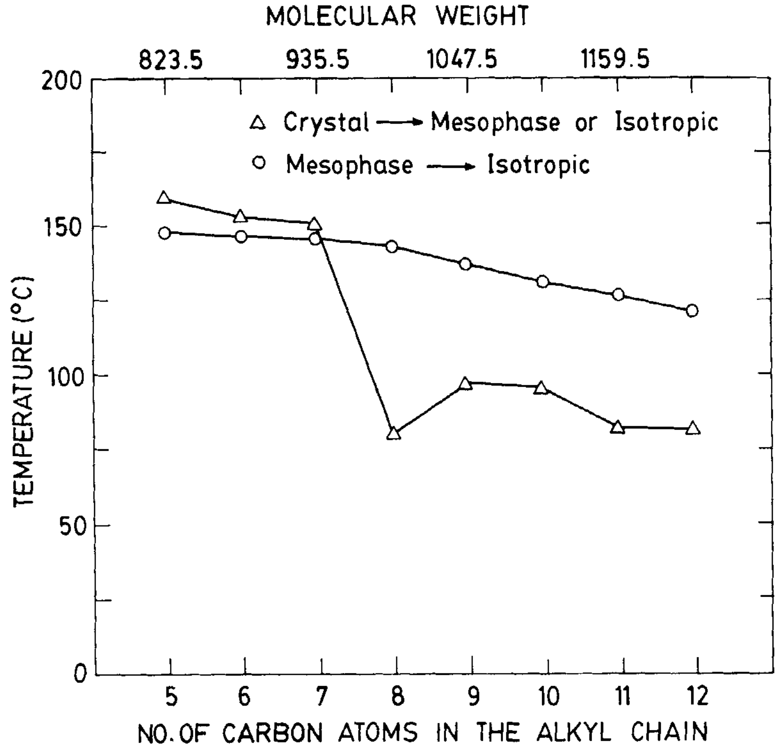


FIGURE 1 A plot of the transition temperatures against the number of carbon atoms in the alkyl chain/molecular weight for a series of bis [1-(*p*-*n*-alkylphenyl)3-(*p*-*n*-alkyloxyphenyl)propane 1,3-dionato]copper(II).

ologues and a broken fan-shaped texture which resembles the smectic C phase, for higher homologues in a series of symmetrically substituted alkoxy copper chelates. Through x-ray diffraction measurements they have identified the mesophase as a discotic lamellar phase in which the molecules tilt with respect to the layers. Our own preliminary x-ray studies of the mesophase have also indicated a layered arrangement of the molecules.

The differential scanning calorimetric data indicate that the mesophase → isotropic transition enthalpies are lower compared with the corresponding crystal → mesophase/isotropic transition enthalpies, though in a few cases they are about the same. The dsc thermogram for compound 17 is shown in Figure 3.

Two homologous series of copper chelates synthesized by K. Ohta *et al.*,[9,12] have been obtained from symmetrical ligands. In other words, they have either four identical alkyl or alkyloxy chains as viewed from the central metal atom. Giroud-Godquin and Billard[11] in their study on discogenic metal complexes have used both symmetrical and unsymmetrical ligands. However, they have not explicitly stated the possibility of *cis/trans* isomerism in unsymmetrical molecules. Their diagram of the metal complex seems to suggest a *cis* isomer. The chelates in the present study are prepared from unsymmetrical ligands and hence can exist as *cis* or *trans* isomers; viz., the two alkyl chains can either be on the same side or on opposite

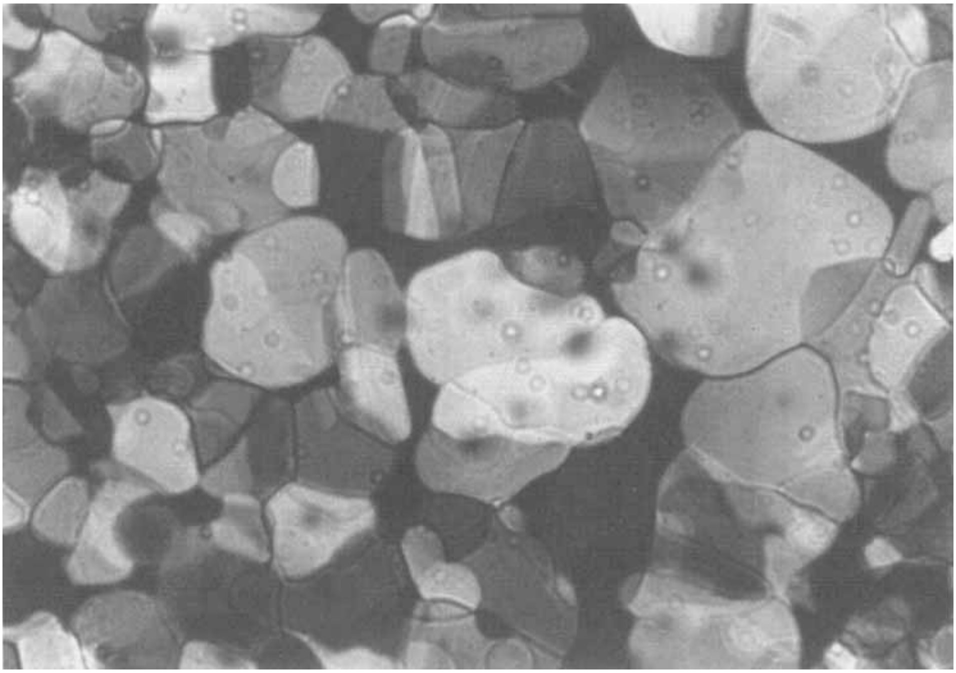


FIGURE 2 The mosaic texture of the mesophases of complex 16 at 129°C (× 350), crossed polarizers. See Color Plate VI.

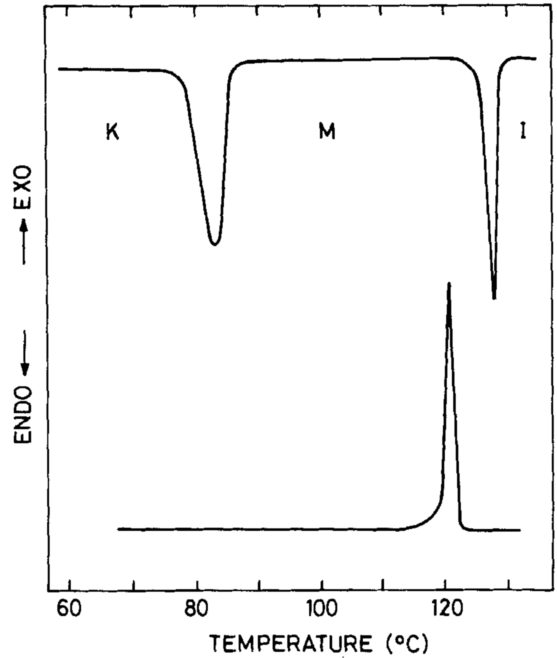


FIGURE 3 Differential scanning calorimetric thermogram of bis[1-(*p*-*n*-undecylphenyl)3-(*p*-*n*-undecyloxyphenyl)propane 1,3-dionato]copper(II), heating and cooling rates 10°/min.

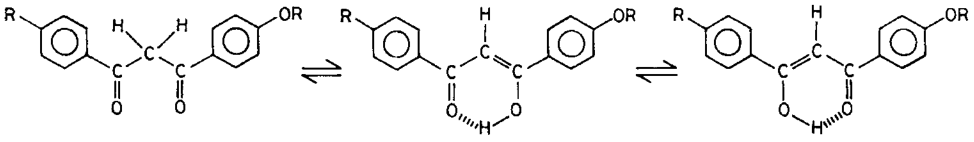


FIGURE 4 Keto-enol tautomerism in β-diketones.

sides. This can be exemplified by considering the tautomeric forms of the ligands as shown in Figure 4. In this figure there is one keto and two enol forms. These tautomers will be in equilibrium with each other and with a suitable cation such as Cu^{++} can complex to give the corresponding chelate. Under slightly basic conditions the enolic forms are favoured and either of these gives the same product namely, the *trans*. However, if these 'enolic' forms are in a 1:1 mixture then probably the product would be 'cis'. The single crystal x-ray study of complex 13 confirms a *cisoid* form. The detailed x-ray analysis of this complex will be reported elsewhere.[15]

To conclude, the metal complexes offer very interesting series of compounds with varying mesogenic properties.

Acknowledgments

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